the coordination sphere is asymmetric with N–N distances 1·15 and 1·21 Å. The valence angle Co–N–N is 120°. From infrared studies Staples & Tobe (1960) have suggested that the valence angle should be in the region 108°–120°. In azidopentamminecobalt azide this angle is 124°. The arrangement of the nitrate ions is interesting; two ions are stacked one above the other at $y=\frac{1}{4}$. Swink & Atoji (1960) have reported such an arrangement in $Ni(en)_3(NO_3)_2$, where the two nitrate ions are stacked one above the other to give close packing with ethylenediamine ions. The NO_3 group is planar. The average N–O distance is 1·24 Å in agreement with the standard empirical value.

The contact distances between non-bonded atoms appear to be reasonable. These distances range upwards from 3·20 Å except for the distance 2·75 Å, between C(2) of the ethylenediamine group and O(2) of the nitrate ion. As the structure is obtained from projection data, no special comment is made regarding this short C–H···O distance.

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The Crystal Structure of Ferricinium Triiodide, $(C_5H_5)_2FeI_3$*

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Ferricinium triiodide crystallizes in the trigonal system with probable space group $R\bar{3}m$. The rhombohedral unit cell has dimensions $a_R=7{\cdot}517\pm5$ Å, $\alpha_R=69°4'\pm10'$ and contains one unit of $(C_5H_5)_2FeI_3$. The trial structure was determined from symmetry considerations and verified by comparison of calculated and observed structure factors for 159 independent reflexions (intensities measured by photometry of precession photographs). Coordinates and Debye–Waller factors of all atoms other than hydrogen were refined by least squares, the final R index being 11·3%. The structure is similar to that of CsCl, but with the unit cell elongated along $[111]_R$. The ferricinium cation is centred at the origin, with the cyclopentadiene rings perpendicular to the threefold axis in a disordered arrangement. The triodide anion is centered at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and lies along the threefold axis. The triodide anion thus appears to be symmetrical and linear, with $d(I-I)=2{\cdot}93\pm0{\cdot}02$ Å. The disorder of the crystal makes it impossible to draw detailed conclusions about the structures of the cation and perhaps the anion. Diffraction photographs at 130°K showed no evidence of a phase change having occurred between 300°K and 130°K.

Introduction

Ferrocene forms a number of compounds with iodine; compositions FcI_n (Fc=ferrocene) have been reported with $3\leq n\leq20$ (Nesmeyanov, Paravahova & Nesmeyanova, 1955; Cais & Adam, 1967). We have carried out a three-dimensional crystal structure analysis of the first member of the series ($n=3$) and the results show that this compound is ferricinium triiodide. The detailed atomic arrangements in ferrocenes and in ferricinium and trihalide ions have been the subject of many investigations, both experimental and theoretical, but disorder in the ferricinium triiodide crystals limits the information that can be obtained from this study about the detailed structures of the ions.

Experimental

Our crystals were prepared (by Mr M. Adam) by solution of FcI_6 in acetone and subsequent slow evaporation of the solvent; black rhombohedra,* stable in air, were deposited. The angles between the faces were $82\pm\frac{1}{2}°$ and the faces were subsequently indexed as $\{110\}_R$.

Oscillation, Weissenberg and precession photographs were taken of crystals mounted about the long diagonal of the rhombohedron (the hexagonal *c* axis) and oscillation and Weissenberg photographs about an axis normal to this diagonal (*i.e.* about the hexagonal *a* axis). Trigonal symmetry was evident from the first set of photographs while the second set showed

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* Based on the M. Sc. thesis of T. Bernstein, accepted by the Senate of the Technion – Israel Institute of Technology, 1967.

* We shall mostly use hexagonal axes in the description of our results; when rhombohedral axes are used, they will be denoted by a subscript $_R$.

that the Laue group was $\bar{3}m$. The systematic absences were compatible with three space groups, of which $R32$ and $R3m$ are non-centrosymmetric and $R\bar{3}m$ has a centre. The referee has suggested that absence of a centre could be detected by exploiting the anomalous scattering of Co $K\alpha$ by the iodine atoms. Appropriate intensity differences were searched for but not found; however it should be noted that absorption corrections were not made.

Accurate cell dimensions were determined with a Stoe back-reflexion Weissenberg camera built following Buerger's (1942) design. The wavelengths assumed for Co $K\alpha$ radiation were:

$$\lambda\ K\alpha_1\ 1{\cdot}79278\ \text{Å} \qquad \lambda\ K\alpha_2\ 1{\cdot}78892\ \text{Å}\ .$$

The results are summarized in Table 1.

The intensities of 159 independent reflexions were measured photometrically from integrated precession photographs (Mo $K\alpha$, Zr filter). The layers photographed were $h0\bar{h}l$, $h1\ \overline{h+1}\ l$ and $h2\ \overline{h+2}\ l$. No corrections were made for absorption ($\mu R \sim 0{\cdot}6$). Lorentz-polarization corrections were applied using an Autocode program for the Elliott 503 computer written by one of us (T.B) on the basis of Waser's (1951) formula. The different layers were put on the same scale by comparison of structure factors of symmetry-related reflexions.

It is shown below that the crystallographic results imply some disorder in the crystals. Oscillation photographs about the [0001] axis taken with Mo $K\alpha$ show bands of diffuse scattering parallel to and encompassing two to three layer lines; their mean spacing is 2·8 Å. However it seems probable that these bands are due to thermal vibrations as they are considerably reduced in intensity when the crystal is cooled to 130°K. The only other difference between corresponding photographs at 300°K and 130°K is the expected slower fall-off in Bragg intensity with angle at the lower temperature. Thus there is no evidence for a phase change between 300°K and 130°K and it was decided to base the structure determination on the more conveniently executed room-temperature measurements. In retrospect it is clear that it would have been better to have measured intensities at a lower temperature.

Determination and refinement of the structure

Three different space groups are permitted by the systematic absences (Table 1) and we must consider what atomic arrangements are compatible with the unit-cell symmetries and atomic sizes. We use hexagonal axes and there are thus three formula units in the unit cell. Firstly, irrespective of space group, the three Fe atoms can be placed in positions (*a*) of the three possible space groups, *i.e.* at the origin and related positions. The cyclopentadiene rings must lie above and below the Fe atoms with the threefold axes running through their centres and normal to the planes of the rings. The cyclopentadiene rings must be disordered to conform to the point group symmetries of positions (*a*) in the three space groups.

There are three possible arrangements for the nine iodine atoms of the three asymmetric units:

(i) in positions of 9-fold multiplicity *i.e.* (*d*) or (*e*) of space groups $R32$ and $R\bar{3}m$, or (*b*) of $R3m$.

(ii) three iodines in a position of 3-fold multiplicity and the others in positions of 6-fold multiplicity *i.e.* (*b*) and (*c*) of $R32$ and $R\bar{3}m$. This possibility does not exist in $R3m$.

(iii) in three different positions of 3-fold multiplicity. This is possible only in positions (*a*) of $R3m$.

The first of these possibilities is eliminated (for all three space groups) because of packing considerations. This arrangement would require that there be equilateral triangles of iodine atoms centred on and normal to the *c* axis and separated by $c/2$ (8·5 Å) from the ferrocene rings above and below. After taking account of the van der Waals radii of these groups there would still be empty regions of thickness 3·2 Å between ferrocene rings and iodine atoms and this arrangement is therefore unacceptable. The second possibility requires that linear and centrosymmetric I_3 groups should lie along the threefold axes between the ferrocene groups. As the point symmetry of I_3 is higher than the point symmetries required by positions (*b*) of the two space groups $R32$ and $R\bar{3}m$ these are thus equivalent so far as the arrangement of the iodine atoms is concerned.

In the third possibility, which applies only to $R3m$, the I_3 grouping must still be linear but not centrosymmetric.

Table 1. *Crystal data*

$C_{10}H_{10}Fe\ I_3$, $M=566{\cdot}66$, $\mu=73{\cdot}2\ \text{cm}^{-1}$ for Mo $K\alpha$.

Trigonal.

Cell dimensions using rhombohedral axes: $a_R=7{\cdot}517\pm5$ Å
$\alpha_R=69°4'\pm10'$

Cell dimensions using hexagonal axes: $a=8{\cdot}522\pm6$ Å
$c=17{\cdot}05\pm1$ Å

Volume of rhombohedral unit cell $=357{\cdot}4\pm7$ Å^3.
$D_m=2{\cdot}55$ g.cm^{-3}, $D_x=2{\cdot}634\pm5$ g.cm^{-3} for one formula unit in the rhombohedral unit cell.

Absent spectra (hexagonal indexing): when $-h+k+l\neq3n$.

Laue group $\bar{3}m$; possible space groups are $R32$ (no. 155), $R3m$ (no. 160) and $R\bar{3}m$ (no. 166).

Thus at this stage it is already possible to establish that the three iodine atoms are collinear and it is reasonable to identify this with a linear triiodide ion. The compound can thus be formulated as ferricinium triiodide. The differences among the structures appropriate to the three possible space groups are clearly small and we proceed on the working hypothesis that the correct space group is that with the highest symmetry, *i.e.* $R\bar{3}m$. It remains to derive the z coordinate of the outer iodine atom of the triiodide ion, a suitable description of the disordered cyclopentadiene rings and the Debye–Waller factors of the various atoms.

An initial position for the outer iodine atom was obtained by assuming $d(\text{I–I}) = 2{\cdot}85$ Å. The atomic coordinates of the outer iodine atom and the anisotropic Debye–Waller factors of the iron and iodine atoms were then refined by least squares using the Daly, Stephens & Wheatley (1965) programming system and the Elliott 503 computer at the Technion. This programming system is based on the method set out by Cruickshank & Pilling (1961). The function minimized is $R' = \Sigma\, w(|F_o| - |F_c|)^2 / \Sigma\, wF_o^2$; the assignment of the weights w is discussed below. The refinement was actually carried out in space group $P\bar{1}$ as computing difficulties were experienced with the refinement in space group $R\bar{3}m$. The higher symmetry was simulated by the inclusion of equal but non-equivalent reflexions as follows (Bertaut & Waser, 1957):

$$F(hkl) = F(k\ \overline{h+k}\ l) = F(\overline{h+k}\ hl)$$
$$= F(\bar{k}\bar{h}l) = F(h+k\ \bar{k}l) = F(\bar{h}\ h+k\ l)$$

The atomic scattering factor for Fe was that given by Freeman & Watson (1961) (self-consistent field with inclusion of exchange); for I the Thomas–Fermi–Dirac values of Thomas & Umeda (1957) were used and for C the SCF values of Hoerni & Ibers (1954). The corrections for anomalous dispersion were obtained from Table 3.3.2C of *International Tables for X-ray Crystallography* (1962).

The carbon and hydrogen atoms were not included in the first stages of the refinement, during which R was reduced to 14% by using anisotropic Debye–Waller factors for the other atoms. These observed and calculated structure factors were then used in the calculation of a three-dimensional difference synthesis which

Table 2. *Coordinates and Debye–Waller factors (in the hexagonal cell) for iron and iodine atoms, and the associated e.s.d.'s*

	x	y	z	$B_a = B_b$ Å^2	B_c Å^2	B_c/B_a
Fe	0	0	0	$3{\cdot}6 \pm 0{\cdot}4$	$1{\cdot}6 \pm 1{\cdot}5$	< 1
I(1)	0	0	$0{\cdot}3267 \pm 6$	$4{\cdot}8 \pm 0{\cdot}16$	$3{\cdot}3 \pm 0{\cdot}6$	$0{\cdot}7 \pm 0{\cdot}15$
I(2)	0	0	$\frac{1}{2}$	$2{\cdot}2 \pm 0{\cdot}16$	$4{\cdot}3 \pm 0{\cdot}6$	$2{\cdot}0 \pm 0{\cdot}4$

The carbon atoms are in a planar ring of radius $r = 1{\cdot}3 \pm 0{\cdot}2$ Å at $z = 0{\cdot}097 \pm 0{\cdot}006$. For reasons given in the text their in-plane coordinates will not be given here in more detail.

Table 3. *Observed and calculated structure factors (hexagonal indices but with i omitted)**

h	k	ℓ	F_o	F_c	h	k	ℓ	F_o	F_c	h	k	ℓ	F_o	F_c	h	k	ℓ	F_o	F_c	h	k	ℓ	F_o	F_c
9	0	0	54	65	1	0	-11	-103	-106	-5	0	-17	-42	-45	2	1	-17	-56	-51	-7	1	-2	52	42
8	0	-1	-40	-47	1	0	-8	36	22	-5	0	-11	-67	-68	2	1	-11	-130	-131	-8	1	-12	60	58
7	0	-11	-36	-41	1	0	-5	-282	-296	-5	0	-5	-121	-120	2	1	-5	-184	-155	-8	1	-6	91	92
7	0	-5	-80	-73	1	0	-2	54	88	-5	0	-2	56	50	2	1	-2	57	43	5	2	-12	78	88
7	0	-2	38	39	0	0	-21	47	55	-6	0	-12	94	100	2	1	1	-217	-194	5	2	-9	37	33
6	0	-18	41	45	0	0	-18	102	103	-6	0	-9	39	42	1	1	-18	93	97	5	2	-6	127	135
6	0	-12	93	99	0	0	-15	51	34	-6	0	-6	134	136	1	1	-15	60	57	5	2	-3	38	35
6	0	-9	41	42	0	0	-12	241	244	-6	0	-3	43	39	1	1	-12	192	205	5	2	0	170	169
6	0	-6	135	137	0	0	-9	204	192	-7	0	-10	44	46	1	1	-9	151	135	4	2	-10	48	56
6	0	0	168	191	0	0	-6	280	313	-7	0	-7	-53	-42	1	1	-6	339	351	4	2	-7	-59	-61
5	0	-10	62	65	0	0	-3	171	171	-7	0	-1	-57	-58	1	1	-3	201	172	4	2	-4	-54	58
5	0	-7	-72	-71	-1	0	-16	53	40	-8	0	-5	-47	-49	1	1	0	352	502	4	2	-1	-111	-97
5	0	-4	68	55	-1	0	-13	-41	-36	7	1	-12	55	59	-3	1	-16	59	64	3	2	-11	-94	-94
5	0	-1	-96	-96	-1	0	-10	138	131	7	1	-6	90	62	-3	1	-10	78	64	3	2	-5	-115	-117
4	0	-17	-69	-48	-1	0	-7	-143	-130	7	1	0	119	111	-3	1	-7	-97	-82	2	2	-18	77	75
4	0	-11	-97	-98	-1	0	-1	-140	-129	6	1	-10	50	51	-3	1	-4	120	100	2	2	-15	61	91
4	0	-5	-138	-129	-2	0	-17	-56	-58	6	1	-7	-48	-48	-4	1	-17	-42	-46	2	2	-12	159	156
4	0	-2	39	47	-2	0	-11	-128	-129	6	1	-1	-71	-64	-4	1	-11	-121	-114	2	2	-9	78	71
3	0	-18	77	80	-2	0	-8	33	16	5	1	-11	-61	-58	-4	1	-5	-159	-128	2	2	-6	311	297
3	0	-15	63	64	-2	0	-5	-247	-198	5	1	-5	-119	-107	-4	1	-2	59	41	2	2	-3	135	127
3	0	-12	171	169	-2	0	-2	79	51	5	1	-2	57	47	-4	1	1	-195	-161	2	2	0	228	309*
3	0	-9	95	83	-3	0	-18	79	82	5	1	1	-106	-82	-5	1	-18	55	57	-5	2	-16	49	48
3	0	-6	304	320	-3	0	-15	69	95	4	1	-18	45	58	-5	1	-15	44	37	-5	2	-10	54	54
3	0	-3	159	146	-3	0	-12	175	167	4	1	-12	162	135	-5	1	-12	142	135	-5	2	-7	-73	-69
3	0	0	354	345	-3	0	-9	103	84	4	1	-9	61	57	-5	1	-9	66	57	-5	2	-4	90	78
2	0	-16	59	58	-3	0	-6	318	323	4	1	-6	238	214	-5	1	-6	251	215	-6	2	-11	-69	-69
2	0	-13	-41	-31	-3	0	-3	170	142	4	1	-3	92	83	-5	1	-3	106	83	-6	2	-5	-97	-104
2	0	-10	101	86	-4	0	-16	48	49	4	1	0	276	260	-6	1	-10	64	61	-6	2	-2	36	45
2	0	-7	-112	-99	-4	0	-10	64	58	3	1	-16	55	56	-6	1	-7	-77	-63	-7	2	-18	38	43
2	0	-4	92	84	-4	0	-7	-86	-76	3	1	-10	64	56	-6	1	-4	61	49	-7	2	-12	86	89
2	0	-1	-135	-185	-4	0	-4	89	80	3	1	-7	-89	-77	-7	1	-11	-45	-45	-7	2	-6	133	135
1	0	-17	-91	-75	-4	0	-1	-160	-140	3	1	-4	112	92	-7	1	-5	-92	-83					

* The values for reflexions 110 and 220 are affected by extinction error.

showed the cyclopentadiene rings in the expected positions. (The distance along [0001] from Fe to ring centre was $1{\cdot}65 \pm 0{\cdot}1$ Å, radius of ring = $1{\cdot}3 \pm 0{\cdot}2$ Å). However, the ring, which was expected to show cylindrical symmetry, in fact had a hexagonal arrangement of peaks. The peak height was 5 e.Å^{-3} while in other regions, the difference synthesis showed peaks of 2 e.Å^{-3} and troughs of -7 e.Å^{-3}. From this it was concluded that the hexagonal appearance of the ring was due to an artifact and not to a particular distribution of ring orientations, and that the measured intensities were not accurate enough to yield any detailed information about the cyclopentadiene rings. For the final calculations of structure factors six atoms, each with $f=\frac{5}{6}f_c$, were placed on the six peaks found in the difference synthesis; the final R value was 11·3%. It is appreciated that this hexagonal arrangement cannot in fact be achieved by superposition of rotated symmetrical five-membered rings. More complicated distributions of the carbon atoms, compatible with the geometrical requirements, did not give improved R values and will not be described. The results from the difference syntheses and structure factor calculations show that the measured intensities are not accurate enough to yield any detailed information about the in-plane orientational arrangement of the cyclopentadiene rings. During the final calculations the weighting scheme was adjusted to minimize the variation of $\langle w\Delta^2\rangle$ with F_o; the best scheme reduced the estimated standard deviations by about 15% below their initial values but there were no significant changes in the atomic parameters.

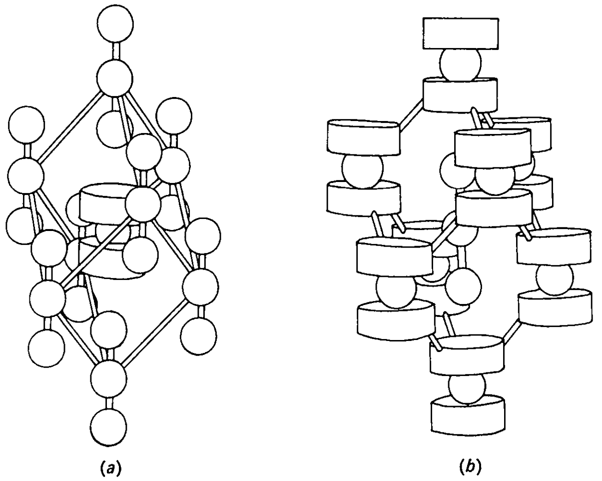
(a) (b)

Fig. 1. Two equivalent representations of the rhombohedral unit cell of ferricinium triiodide. In (*a*) the origin is taken at the centre of the anion and in (*b*) at the centre of the cation. In space groups $R\overline{3}m$ and $R32$ the centre of the cation in (*a*) (anion in (*b*)) is necessarily at the centre of the unit cell but this will not be so for $R3m$.

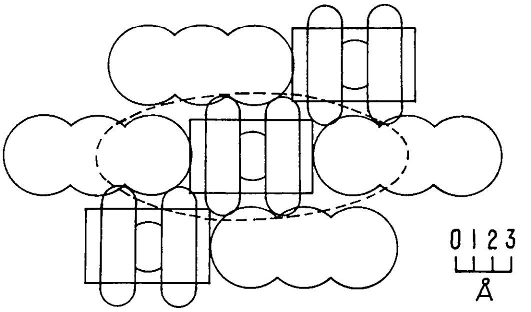

Fig. 2. Section through the (11$\bar{2}$0) plane, showing how the arrangement can be represented by close-packed ellipsoids. The values used in the diagrams are d(C–H) = 1·1 Å, van der Waals radii of iodine, carbon and hydrogen 2·15, 1·7 and 1·0 Å respectively.

The final parameters obtained from refinement in $R\overline{3}m$ (actually $P\overline{1}$ as explained above) were refined in $R3m$ (actually in $P1$) but no significant changes were found. Thus it was concluded that, in terms of the experimental data and computing programs at our disposal, there was no reason to doubt that the correct space group was $R\overline{3}m$.

Results

The final atomic coordinates and Debye–Waller factors are given in Table 2 and the corresponding observed and calculated structure factors in Table 3. The atomic arrangements are shown in Figs. 1 and 2.

We must now consider how the finer details of the results could be altered if one of the space groups $R32$ or $R3m$ is in fact correct. The space groups $R32$ and $R\overline{3}m$ differ only in the point symmetry assigned to the disordered ferricinium ions. In the space group $R3m$ the centre of symmetry of the ferricinium ion is not preserved nor is the overall symmetry of the arrangement of cations and anions. So far as the ferricinium ions are concerned, the differences affect only the locations of the disordered carbon atoms and the present intensity measurements are not accurate enough to permit a choice among the three possibilities. So far as the triiodide ions are concerned, the space groups $R\overline{3}m$ and $R32$ are equivalent but differ from $R3m$ where the triiodide ion will be unsymmetrical; the I_3^- ion will be linear in all three space groups.

The Debye–Waller factors of the iodines determined in space group $R\overline{3}m$ do suggest that there is a disordered arrangement of unsymmetrical triiodide ions. The values of B_a and B_c for I (1) and B_a for I (2) can be interpreted in terms of a rigid body translation (along [0001]) and libration (about [10$\bar{1}$0] and [12$\bar{3}$0] say) but this does not account for the large value found for B_c of the central iodine atom I (2). A reasonable explanation is that this atom is in fact distributed over two off-centre on-axis positions. It is also feasible that the apparent librations are partly due to a disordered arrangement of slightly bent I_3^- ions, atoms I(1) and I(3) being slightly displaced off the trigonal axis. This latter type of disorder could occur in all three possible space groups.

Discussion

(*a*) *The triiodide anion*

Trihalide anions, both unmixed (*e.g.* I_3^-) and mixed (*e.g.* IBr_2^-, ICl_2^-) have been the subject of considerable experimental and theoretical study and the most recent results have been summarized and discussed by Migchelsen (1967) and Migchelsen & Vos (1968). Both unsymmetrical and symmetrical trihalide ions have been found and this has been explained semi-quantitatively by Migchelsen & Vos (1968) in terms of the influence of the surrounding electrostatic field on the anion, as suggested earlier by Hach & Rundle (1951), Havinga & Wiebenga (1959) and Brown & Nunn (1966). The overall length of both symmetrical and unsymmetrical triiodide ions is 5·87 Å in all the crystals for which accurate results are available; this is not in accord with Slater's (1959) theory, which requires a dependence of internal dimensions on overall length. In some crystals the I_3^- ions deviate from linearity by up to 4° but this small effect has not been discussed theoretically.

The I–I distance in the symmetrical anion of ferricinium triodide (2·93, e.s.d. 0·02 Å) is equal to that found in the symmetrical anion of polymorph I of $(C_2H_5)_4NI_3$ (2·935, e.s.d. 0·0018 Å) (Migchelsen & Vos, 1968). Although there appears to be some evidence for disordered packing of unsymmetrical anions in ferricinium triiodide, examination of the Debye–Waller factors of polymorph I of $(C_2H_5)_4NI_3$ does not show any similar effect. More accurate intensity measurements at low temperatures will be required in order to determine whether the apparent symmetry found for some I_3^- ions is a real effect or an artifact due to disorder in the crystals. However, other techniques may be more sensitive than X-ray diffraction: for example pure quadrupole resonance has recently been used (Sasane, Nakamura & Kubo, 1967) to demonstrate the inequivalence of the iodine atoms in the triiodides of ammonium, rubidium and caesium, in agreement with the crystallographic results (Mooney, 1935; Tasman & Boswijk, 1955).

(*b*) *The ferricinium cation*

The present results show that the cyclopentadiene rings of the ferricinium cation are rotationally disordered but it is not possible to state whether this is due to an intramolecular 'free' rotation of the rings within the ion or to a disordered arrangement of rigid ions.

(*c*) *Packing of the ions*

The ionic arrangement is shown in Figs. 1, 2 and 3. As Wells (1962) has emphasized, it is essential to take into account the value of the rhombohedral angle when considering whether apparently isomorphous crystals are indeed isostructural. When this is done it appears (Wells, 1962) that, of the MXY_2 crystals investigated, only $CsICl_2$ (Wyckoff, 1920) is isostructural with ferricinium triiodide.

The packing is compact. If the ellipsoid of revolution shown by a broken line in Fig. 2 is taken as the packing unit, then the arrangement is an example of the densest packing of ellipsoids derived from cubic close packing of spheres by an affine transformation (Matsumoto & Nowacki, 1966). Alternatively the crystals can be described as having the *B*2 structure (CsCl type) distorted by elongation in the direction of $[111]_R$.

Each ferricinium cation is surrounded by eight triiodide ions; two of these are above and below the cations, with $d(\text{Fe}\ldots\text{I}) = 5{\cdot}59$ Å and the other six are almost in the same plane as the iron atom and 4·92 Å away from it (Fig. 3). These iodines are all outer atoms of the triiodide ions. It has been suggested (Brown & Nunn, *loc. cit.*) that these outer iodines carry most of the ionic charge; it is also usual to consider that the positive charge of the ferricinium ion is located on the iron atom (Zahn, Kienle & Eicher, 1962). Thus this arrangement would be expected to be especially stable. However it should be noted that it can equally well be considered to be a consequence of the chance near-equality between the overall length of the triiodide ion and $d(\text{Fe}\ldots\text{I})$ in the direction of [0001].

The closest approach between iron and iodine is 4·9 Å (Fig. 3) and it is interesting to note that Brand & Sneddon (1959) calculated this value for $d(\text{Fe}\ldots\text{I})$ in solutions of ferricinium iodide on the basis of Bjerrum's theory of ionic association.

Conclusions

The principal conclusions from the present crystal structure analysis are that the compound examined is ferricinium triiodide and that the cations and perhaps the anions are disordered in the crystals.

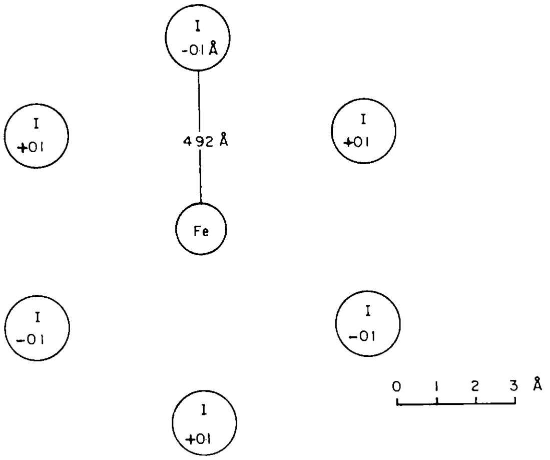

Fig. 3. Section through the (0001) plane showing the arrangement of iodines about the iron of a ferricinium ion. The displacements of the centres of the iodine atoms from their mean plane is shown.

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The Crystal and Molecular Structure of Azobenzene-2-Sulphenyl Cyanide

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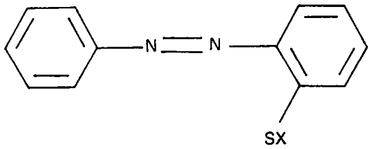
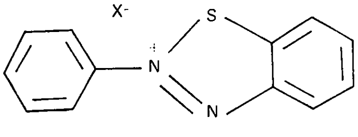
Azobenzene-2-sulphenyl cyanide, $C_6H_5N{:}NC_6H_4SCN$, crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell of dimensions $a=12{\cdot}99$, $b=22{\cdot}01$ and $c=3{\cdot}79$ Å. The structure has been determined from two-dimensional X-ray intensity data. The approximate structure has been obtained by optical-transform methods in conjunction with a Patterson projection and has been refined by Fourier and difference Fourier syntheses. The non-ionic nature of the S–CN linkage in the crystalline state of azobenzene-2-sulphenyl cyanide has been established, supporting the findings of the absorption spectra of the compound in the ultraviolet and visible regions. The refined structure has shown that the molecule is non-planar.

Introduction

Important features of structural interest in azobenzene-2-sulphenyl derivatives, which form a special group of compounds within the *ortho*-mercaptoazo compounds, have been pointed out by Burawoy, Liversedge, Vellins, Bartindale & Farrow (1954). A detailed analysis of ultraviolet and visible-light absorption spectra of these compounds made by these workers, using different solvents, has suggested structure (I) for non-ionic, and structure (II) for ionic members of the series. It is also suggested that in the case of halides there are indications of an equilibrium between ionic and non-ionic isomers in solution. These findings, however, do not throw any light on the structures of azobenzene-2-sulphenyl derivatives in the solid state. With the exception of a preliminary study of the structure of azobenzene-2-sulphenyl chloride (Burawoy *et al.*, 1954:



(I)



(II)